

PATENT SPECIFICATION

DRAWINGS ATTACHED



851202

Date of Application and filing Complete Specification Oct. 9, 1958.
No. 32202/58.

Application made in United States of America on Oct. 9, 1957.
Complete Specification Published Oct. 12, 1960.

Index at acceptance:—Class 53, BD(8A:8F:8K:9D:10C:12), BP(1A:1C:2B1:3A4:3C:4B:4D)
BS(1A3:1A13:1A15:1D4:3A1:3C:4B).

International Classification: —H01m.

COMPLETE SPECIFICATION

Improvements in and relating to Electric Dry Cells

We, UNION CARBIDE CORPORATION, of 30, East 42nd Street, New York, State of New York, United States of America, a corporation organised under the laws of the State of New York, United States of America, (assignee KARL KORDESCH) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is generally concerned with rechargeable dry cells, and more particularly with dry cells employing an oxidic depolarizer in conjunction with an alkaline electrolyte. The invention especially relates to a dry cell of the character indicated, which is adapted to be electrically recharged by passing therethrough a direct current having a voltage greater than its internal electromotive force, and in opposition thereto.

The prior art is amply supplied with suggestions and proposals for recharging LeClanche-type cells. Strictly speaking, these have not been successful, primarily because the occurrence of irreversible reactions in the manganese dioxide, ammonium chloride zinc system presented problems which could not be solved. Among such problems are the failure of certain cell-produced precipitates to decompose when contacted with charging current and the disintegration of the cathode upon discharge.

It has been found, in accordance with the present invention, that a system employing an oxidic depolarizer, a zinc anode and an alkaline electrolyte can be utilized in the construction of a dry cell, which may be recharged many times during the life thereof without appreciable reduction in its high capacity to volume ratio.

The dry cell of the present invention has a low internal resistance, which is retained throughout the life thereof. It can also perform advantageously with an inexpensive low grade

manganese dioxide depolarizing mix.

In the accompanying drawings, Fig. 1 represents a cross-sectional view of the cell of the invention;

Fig. 2 is a cross-sectional view of a separator used in the cell of Fig. 1.

Figs. 3, 4 and 5 are graphs showing performance data of the cell of Fig. 1, and

Fig. 6 is a partial side elevational view showing details of a variant of the invention particularly suitable for heavy duty use.

According to the present invention, a rechargeable dry cell comprises a metallic container serving as the positive terminal thereof, a cathode in the container, an elastic spacer separating the lower end of the cathode from the bottom of the container and normally defining an expansion space between the lower end of the cathode and the container bottom, finely divided anodic particles mixed with an alkaline electrolyte, a separator disposed between the anodic particles and the cathode, an anode collector in contact with the anodic particles, an elastic spacer resting on top of the cathode, a closure for the container, an expansion space intermediate the elastic spacer and the closure, and contact means passing through the closure and elastic spacer to contact the anode collector.

Referring now to Fig. 1, there is shown a cell comprising a cylindrical steel container 10 serving as the positive terminal thereof. As indicated, this container has an open end and a bottom integral therewith, having a protuberance 12 provided with a blow-out safety vent 14. Fitting snugly within the container is a cylindrical molded, cement bonded cathode 16, separated from the bottom thereof by a gas permeable elastic spacer 18, normally disposed in a curvi-linear manner as shown in order to define an expansion space 20 for cell reaction by-products.

With the previously described elements in place, the next step in assembling the cell of

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BS(1A3:1A13:1A15:1D4:3A1:3C:4B).

International Classification: —H01m.

COMPLETE SPECIFICATION

Improvements in and relating to Electric Dry Cells

ERRATA

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SPECIFICATION NO. 851,202

Page 2, line 30, for "32202/58" read "32201/58"

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Page 2, line 78, after "as" insert "a"

Page 2, line 98, for "LeClanche" read "Le Clanche"

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Page 3, line 27, after "half" insert "of"

Page 3, line 62, after "particles" insert "and the cathode an anode collector in contact with the anodic particles"

20 THE PATENT OFFICE,
26th June, 1961

DS 93515/1(13)/P.153 200 6/61 PL

gestions and proposals for recharging LeClanche-type cells. Strictly speaking, these have not been successful, primarily because 25 the occurrence of irreversible reactions in the manganese dioxide, ammonium chloride-zinc system presented problems which could not be solved. Among such problems are the failure of certain cell-produced precipitates to decompose when contacted with charging current and the disintegration of the cathode upon discharge.

It has been found, in accordance with the present invention, that a system employing an 35 oxidic depolarizer, a zinc anode and an alkaline electrolyte can be utilized in the construction of a dry cell, which may be recharged many times during the life thereof without appreciable reduction in its high capacity to volume ratio.

The dry cell of the present invention has a low internal resistance, which is retained throughout the life thereof. It can also perform advantageously with an inexpensive low grade

posed between the anodic particles and the cathode, an anode collector in contact with the anodic particles, an elastic spacer resting on top of the cathode, a closure for the container, an expansion space intermediate 60 the elastic spacer and the closure, and contact means passing through the closure and elastic spacer to contact the anode collector.

Referring now to Fig. 1, there is shown a cell comprising a cylindrical steel container 10 serving as the positive terminal thereof. As indicated, this container has an open end and a bottom integral therewith, having a protuberance 12 provided with a blow-out safety vent 14. Fitting snugly within the container is a cylindrical molded, cement bonded cathode 16, separated from the bottom thereof by a gas permeable elastic spacer 18, normally disposed in a curvi-linear manner as shown in order to define an expansion space 20 for cell reaction by-products.

With the previously described elements in place, the next step in assembling the cell of

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the invention is to insert a separator bag 22, preferably consisting of three layers of material, as will be described hereinafter. The separator is closed at the bottom, and may
 5 be closed at the top. A copper screen anode collector 24 is then placed in the center of the cell, and the space remaining therearound is filled with powdered zinc 25 coated with carboxy methyl cellulose. Alkaline electrolyte is
 10 then poured on this powder. After no more free liquid appears on top of the powder, the separator bag is folded together over the top of the powder. A circular gas permeable elastic spacer 26 is then placed in the cell with
 15 its outer periphery resting on top of the cathode and with its center pressing downwardly toward the top of anode collector 24, so as to define an expansion space 28 between the spacer and the plastic closing disk 30,
 20 which completely seals the cell so as to prevent escape of oxygen therefrom. A copper wire 32 in contact with the anode collector passes through the plastic closing disk and spacer 26 and is soldered at 33 to a negative terminal
 25 plate 34 crimped into disk 30. The cell is suitably closed by crimping the ends of the

steel container over the closing disk 30 as shown at 36 and 38.

In general, the cathode is one as claimed in co-pending Application No. 3220/58 (Serial No. 851,201) and comprises:—

100 grams - Electrolytic manganese dioxide
 20 grams - Graphite
 10 grams - Portland cement
 5 grams - Steel wool

35 12 millilitres 9 Normal potassium hydroxide

Inclusion of the steel wool in these cathodes is optional. As much as 40 grams of graphite may be used with the 100 grams of manganese dioxide. Similarly, instead of electrolytic manganese dioxide, low grade ore may be used.

40 The capacity of the cell anode exceeds that of the cathode by about 50 per cent. The cylindrical amalgamated copper screen 24 which serves as anode collector prevents the consumption of zinc inside the screen. Unchanged powdered zinc is then left as a basis for recharging even after a great many cycles. A typical formulation of an anode suitable for the cell of the invention is as follows:—

	150 grams	Powdered zinc (through 35 to 100 mesh, 4 per cent amalgamated)
55	5 grams	Sodium carboxy methyl cellulose, high vis- cosity
	75 millilitres	Water

In the preparation of the anode, the above components are thoroughly mixed, extruded into thin sheets and dried. The dry material is later crushed to a particle size between 10 and 20 mesh. About 10 ml. of 9 normal potassium hydroxide is added to the crushed material to form a gel. It is necessary in the cell of the invention that the anode be inserted therein in gel form. Such a physical state prevents the setting out of small zinc particles. This has been found to be especially important with recharged zinc, which usually has the appearance of fine powder sticking to larger zinc particles left over from the original zinc material. In addition, the gel reduces zincate ion migration, as well as the possibility of free zinc formation.

As shown in Fig. 2, the separator used in the cell of the invention preferably consists of three layers, and resembles a bag. The middle layer may be a semi-permeable membrane, such as non-fibrous semi-permeable membrane made of cellulose acetate. Preferably, the two layers can be made from a copolymer of acrylonitrile and vinyl chloride "Vinyon" (a Registered Trade Mark). The excellent wet strength of the two Vinyon layers protects the softer non-fibrous membrane material from mechanical damage caused, for example, by steel wool, whiskers or sharp zinc particles.

Performance data for the present cell will

be described by pointing out its behaviour upon heavy current discharge and light current discharge. Fig. 4 shows the cycling performance of a "D"-size cell of the invention on heavy current discharge. For this determination, an 0.5 ampere current was rated as a reasonably heavy discharge current for a "D"-size cell, as it was continuously drawn for a period of six hours. By comparison with the cell of the invention, a Leclanche cell of the same size would carry this load for about three hours only with a far wider voltage spread. The total capacity of the cell of the invention under this discharge was 8 to 10 ampere hours. It is advantageous, however, for the cycle life of a cell to take only 30 percent of its rated capacity out, and recharge afterwards. Naturally its full capacity is always available at the cost of further rechargability. A fresh cell has a total capacity of about 8 ampere hours; with a cell which had been cycled 20 times, a total of about 4 to 5 ampere hours remains to a cut-off voltage of 0.75 volts.

Referring now to the curves of Fig. 3, it can be seen that during the first five cycles, cells were charged to a potential of 1.70 volts with the current on, and for the next five cycles the cells were removed from the charger at 1.60 volts. The result was a lower starting voltage, but also a lower end voltage at discharge. The curves shown represent the aver-

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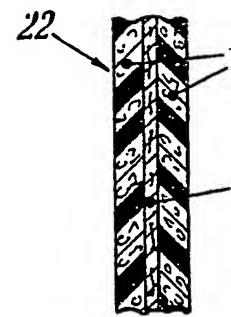
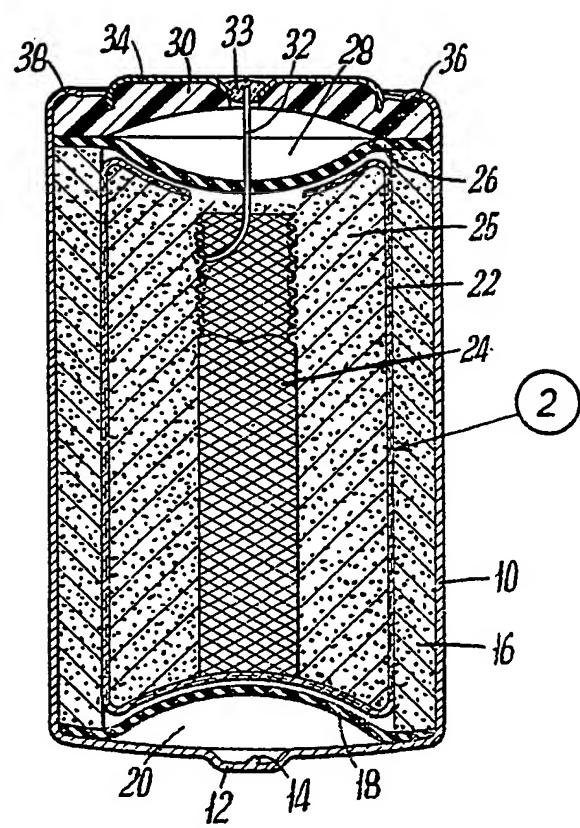
115

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- age values of four cells. After the tenth cycle, the cell resistance variation ranged between 0.15 ohm and 0.30 ohm. 60
- If the cell is left on load after its cathode is exhausted, the surplus zinc which is still left goes into solution with hydrogen evolution on the cathode. This effect starts at a cell voltage of under 0.4 volts. For this reason a safety vent is incorporated in the cells.
- Fig. 5 shows the cycling performance of the cells of the invention on so-called light duty or "trickle" charge. In this type of test, the cells were discharged with a current of 0.2 amperes for 16 hours. The discharge-charge cycles were repeated a number of times and the curves of the drawing reproduce the charging curves for the third cycle and the twentieth cycle. Thus starting with a 16 hour discharge period, 1/3 of the initial capacity of the cell was reserved, and from then on the discharge trickle charge cycles were begun. After a total of 110 hours of service on load, the final discharge was made to determine the remaining capacity. The result indicates that the trickle charging procedure kept the batteries in a state of charge corresponding to about half the fresh cell capacity. Parallel cycling experiments which started with fresh cells ended at about the same level as the initially 1/3 discharged cells. 70
- The ampere hour efficiency of the charge cycles shown in Figs. 4 and 5 (0.5 ampere discharge for six hours, 0.2 ampere charge for 16 hours) is quite good, essentially over 80 per cent. 75
- Research leading to the foregoing developments and results established that the investigated cell system produces oxygen gas at its cathode if kept on charge too long, and that oxygen thus generated can oxidize the anode, if given access thereto. By means of the arrangement of Fig. 6, any oxygen produced on overcharge can easily reach a sufficiently large zinc powder area, and a pressure build-up within the cell is avoided or at least reduced. This is achieved by inserting in the anode collector cylinder 24, a polyethylene sponge cylinder 40 made extremely electrolyte repellent by dipping in a 1½ per cent paraffin-petroleum ether solution followed by air drying. 80
- WHAT WE CLAIM IS:—**
1. A rechargeable dry cell comprising a metallic container serving as the positive terminal thereof, a cathode in the container, an elastic spacer separating the lower end of the cathode from the bottom of the container and normally defining an expansion space between the lower end of the cathode and the container bottom, finely divided anodic particles mixed with an alkaline electrolyte, a separator disposed between the anodic particles, an elastic spacer resting on top of the cathode, a closure for the container, an expansion space intermediate the elastic spacer and the closure, and contact means passing through the closure and elastic spacer to contact the anode collector. 85
 2. A dry cell as claimed in Claim 1, in which the container is made of steel. 90
 3. A dry cell as claimed in Claim 1 or 2, in which the container has an open top and an integral bottom, having a protuberance provided with a blow-out safety vent. 95
 4. A dry cell as claimed in Claim 3, in which the protuberance serves as a contact means. 100
 5. A dry cell as claimed in any one of the preceding claims, in which the cathode is composed of graphite and manganese dioxide and is bonded by means of cement. 105
 6. A dry cell as claimed in any one of the preceding claims, in which the cathode is composed of manganese dioxide, graphite, steel wool and potassium hydroxide and is bonded by means of cement. 110
 7. A dry cell as claimed in any one of the preceding claims, in which the anode is in gel form. 115
 8. A dry cell as claimed in any one of the preceding claims, in which the anodic particles are zinc particles coated with carboxy methyl cellulose. 120
 9. A dry cell as claimed in any one of the preceding claims, in which the separator consists of three layers, the middle one being a semi-permeable membrane and the other two a copolymer of acrylonitrile and vinyl chloride. 125
 10. A dry cell as claimed in any one of the preceding claims, in which the anode collector is composed of copper. 130
 11. A dry cell as claimed in any one of the preceding claims, in which the anode collector is a screen cylinder. 135
 12. A dry cell as claimed in Claim 11, in which the screen cylinder contains an electrolyte-repellant polyethylene sponge. 140
 13. A rechargeable dry cell, substantially as hereinbefore described with reference to and as illustrated by Figures 1 or 6 of the accompanying drawings. 145

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12, Church Street, Liverpool, 1,
Chartered Patent Agents.

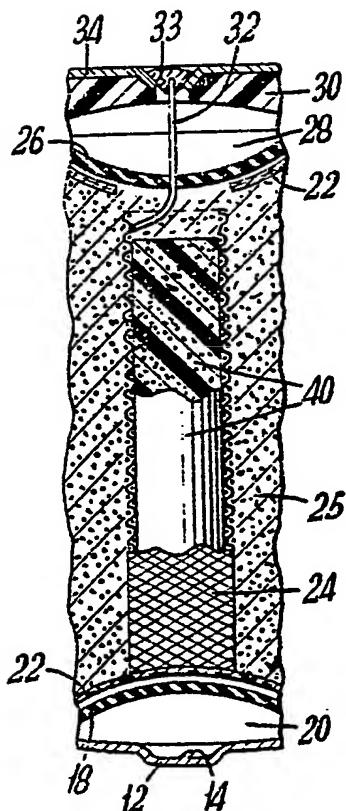
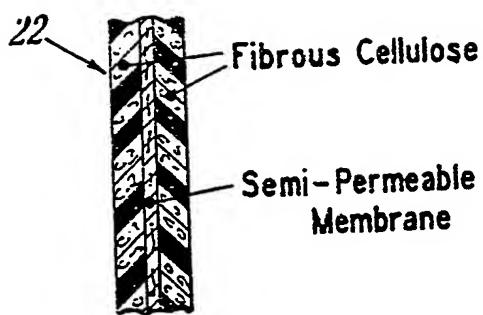
Fig. 1.



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Fig. 1.

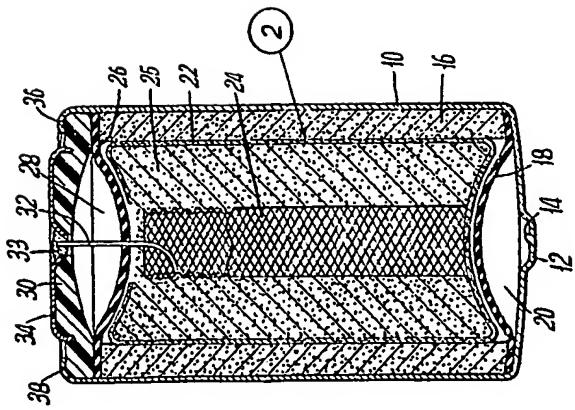


Fig. 6.

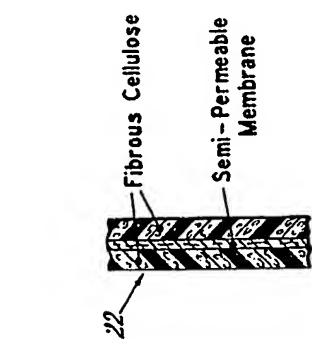
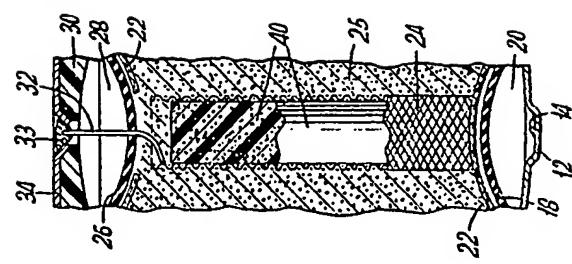


Fig. 2.



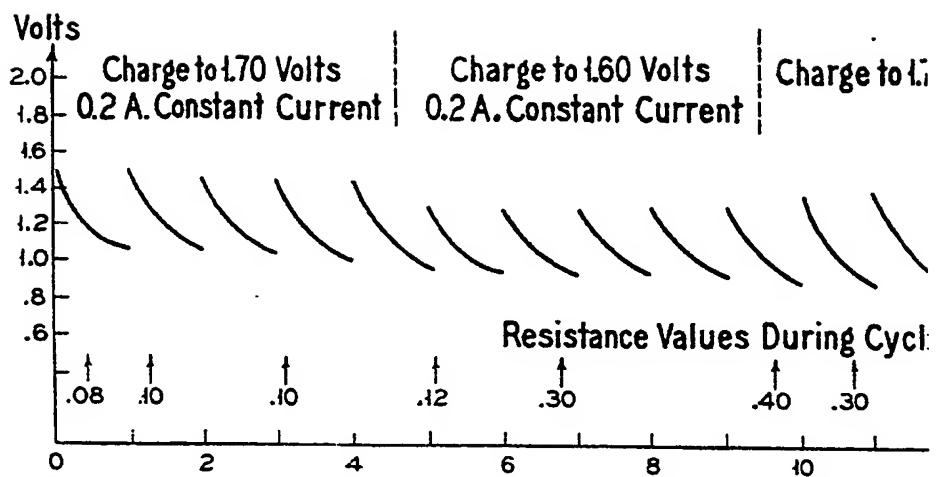
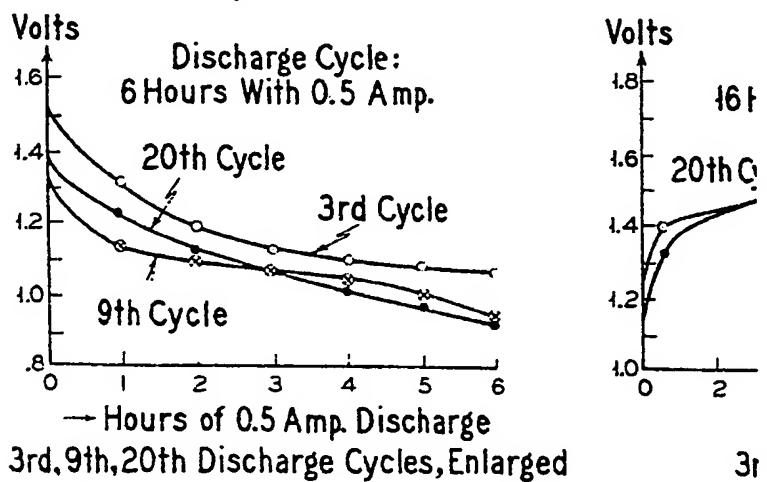


Fig. 3.

Fig. 4.



3rd, 9th, 20th Discharge Cycles, Enlarged

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SHEET 2

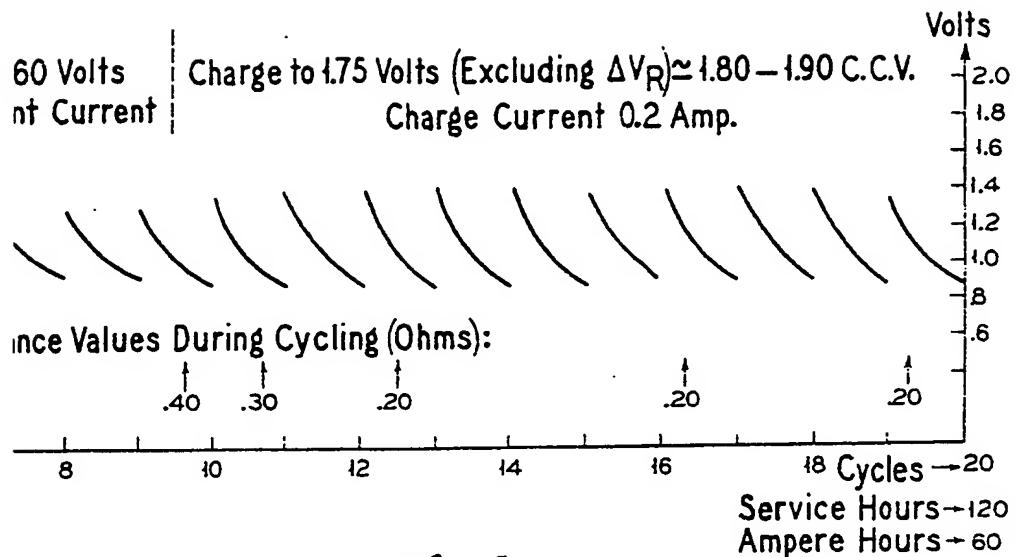
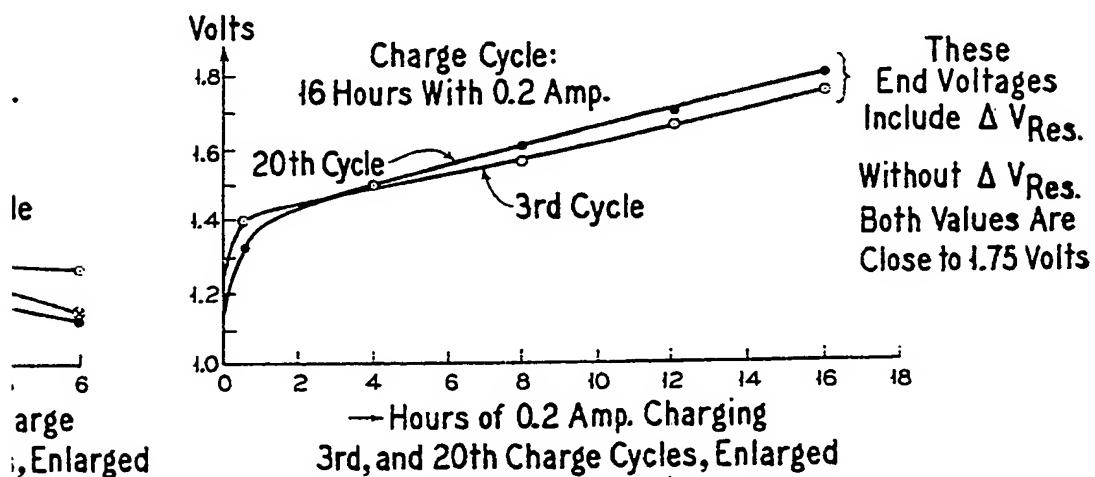


Fig. 5.



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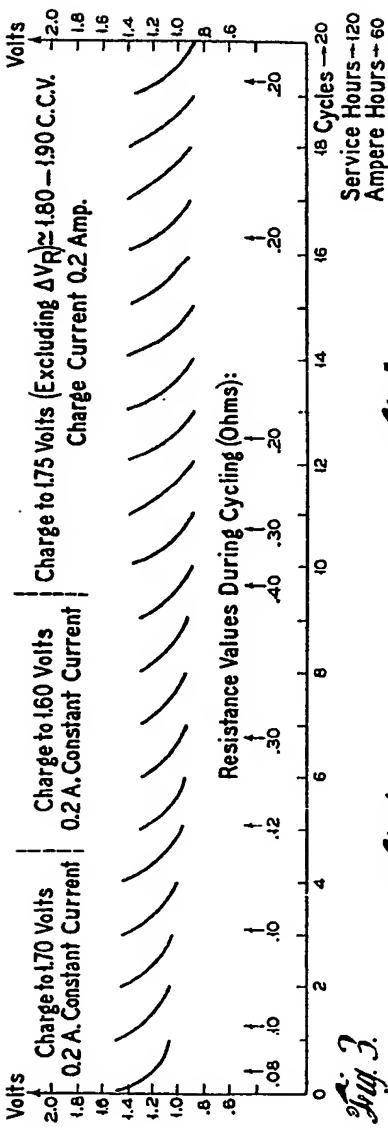
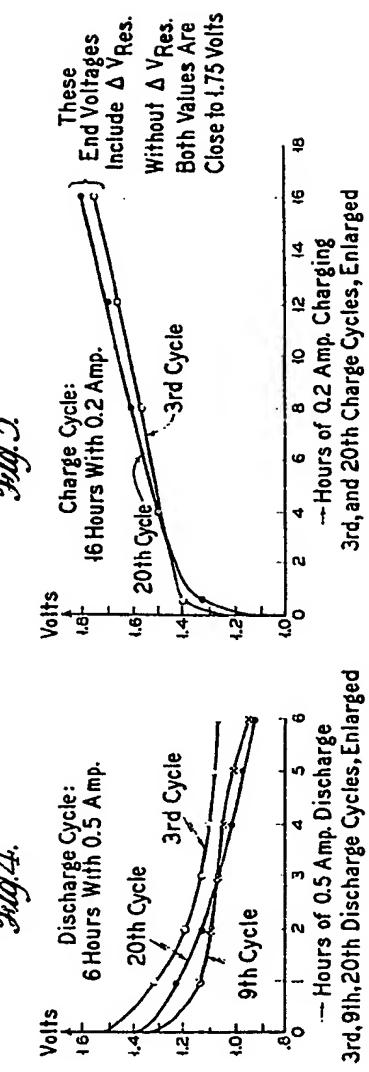


Fig. 3.



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